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Universal current–potential relationship for mass-transfer through Formal Graph approach

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Abstract

The Formal Graph theory, a new language able to model graphically instead of algebraically most of basic equations used in physics and chemistry, is applied to mass-transfer occurring in electrochemical reactions. The integral admittance used in electrodynamics is generalized to all domains where energy is defined. Associated with the concept of energy coupling, this leads to very simple relationships between variables and operators describing processes in a system containing several energy varieties. The paradox of two different forms for the electric capacitance, linear in electrostatics and exponential in electrified materials, is treated and understood. The concept of energetic path brings physical meaning into mathematical models by attributing to each link a role in the conservation or dissipation of the energy. Normal transient diffusion, featured by an exponent 1/2, conserves half of energy, while anomalous diffusion, featured by an exponent p different from 1/2, conserves only 100 p%. The principle of every electrochemical measurement is represented in a simple and clear way by associating two Formal Graphs. The use of a mass-transfer operator generalizing all kinds of mass-transfer (diffusion, convection, thin layer, etc.) and for all geometric situations, allows the characterization of unknown process without previous knowledge of an algebraic model.

Keywords: Formal Graph; Admittance; Mass-transfer; Anomalous diffusion; Energy coupling

1. Introduction

In analytical electrochemistry, several methods for characterizing electroactive substances and oxido-reduction mechanisms exist, each one having its genuine advantage and drawback. The art of the electroanalyst is to choose among them the most adapted method to a specific problem, having to find the necessary compromise between experimental sophistication and mathematical complexity of the interpretation. For historical reasons, each method has developed its own mathematical treatment and there is no unity among the various available models.

Inside each method is found another division. According to the nature of the unavoidable mass-transfer (or adsorption) step in an electrochemical mechanism, migration, diffusion, stationary transport, and so on, one has to use different models that may eventually present more or less approximations or simplifications. These are concerning the symmetry of the electrode and of the cell, the identity between diffusion coefficients, the reversibility of the kinetics, etc. When all these variable elements are known in advance, when one can assume that the mass-transfer is a well-defined type, such as transient semi-infinite diffusion for instance, the choice of a suitable model is not a problem.

A difficulty arises when the mass-transfer does not fulfil the requirement of any model or when its nature is not accurately known, or may evolve during the experiment. The lack of general model is a methodological issue and an obvious source of errors and misinterpretations. A second difficulty may come with the physical interpretation in case of anomalous transfer, such as fractal diffusion that is commonly modelled by a constant phase element (CPE) in equivalent circuits. This purely mathematical being does not allow a meaningful understanding of the process and is quite frustrating in expressing our inability to go further.

The present work is aiming at enhancing the situation in proposing a universal model for all methods and mass-transfers,

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based on a physical approach, allowed by the use of a new theoretical tool called Formal Graph [1].

It consists in a new language, using a graph representation for modelling relationships between physical and chemical variables, able to replace the ordinary algebra commonly used. Similar structures are emerging from the application of this tool to various scientific domains, in fact every branch in which the concept of energy is used and quantified. From this observation, new possibilities for understanding analogies and discrepancies are offered to the theoretician. The elaboration of a theory (a grammar), based on the first principles of thermodynamics, is then the following step, offering a new approach of physics and (physico-) chemistry. Only a first introduction of this new language is presently published [1], the remaining part being in preparation.

This paper unfolds some results, without too many demonstrations, that are able to receive attention from electrochemists looking for a more unified view of their domain. Some of them have been the object of a brief account [2]. Among the subjects that this new theory tackles is the key question of the different forms of the electric capacitance, which is most of the time taken as defining a linear relationship between potential and charge ($Q = CV$) and sometimes as defining an exponential function of the potential for an ionic population (Boltzmann distribution in charged layers for example). The graphs that are drawn in each domain, electrodynamics and physico-chemistry (and many others) exhibit identical structures that suggest a common identity also in the functions relating the various variables. Based on this observation, a general model for the capacitance is given, and on the same idea, a general expression for the admittance is given that covers all cases.

In addition to the comparison of structures, a graph possesses an interesting feature that ordinary algebra has not, which is the path between nodes. Provided a judicious choice of rules for building them, each elementary path in a Formal Graph is shown to correspond to a specific way for the energy in the system to be stored, dissipated, distributed or converted. This enlightens the understanding of many processes, among them the various mass-transfers encountered in electrochemistry.

After having defined the generalized admittance and exposed the basic properties of a Formal Graph, the concept of energy coupling will be introduced as the mean to take into account the coexistence and interactions of different energy varieties in a system. This will be utilized for introducing the notion of influence of an energy coupling upon the function that governs the capacitance and later, for describing the principle of an electrochemical measurement in terms of characterization of an electrical property for a process that involves another energy variety. Before this last point, the various types of mass-transfer and their models will be reviewed, the way of representing them in a Formal Graph depicted and the concept of generalized mass-transfer operator introduced. Analysis of the paths found in the graph will finally lead to the formulation of the general admittance, useful in ac modulation technique such as impedancemetry, but not only, since it will be shown that this operator may be used for large signal techniques too (cyclic voltammetry and others). General potential–current and potential–charge relationships valid for all methods will be deduced and an expression for evaluating the operator representing an unknown mass-transfer will be proposed.

2. Definition of the generalized admittance

In electrodynamics, the admittance $\hat{\mathbf{Y}}$ is an operator linking the electric potential to the current

$$\text{admittance,} \quad i = \hat{\mathbf{Y}} V \tag{1}$$

It should not be confused with the differential admittance

$$\text{differential admittance,} \quad \mathrm{d}i = Y\,\mathrm{d}V \tag{2}$$

corresponding to the derivative of the admittance at a given functioning point, mainly used in ac-impedancemetry. The same distinction, integral–differential, works naturally for the reciprocal of the admittance, the impedance $\hat{\mathbf{Z}}$, defined as

$$\text{impedance,} \quad V = \hat{\mathbf{Z}} i \tag{3}$$

$$\text{differential impedance,} \quad \mathrm{d}V = Z\,\mathrm{d}i \tag{4}$$

In its integral form, the admittance or impedance operator describes in fact every relationship between an electric potential and a current simultaneously measured. Any electrochemical measurement amounts to the determination of such an operator, whatever the shape (time dependence) and the magnitude of the imposed signal, current or potential. It is important to emphasize that cyclic voltammetry, among other methods, provides a measure of an admittance or impedance, because unhappily the electrochemical literature systematically reduces the term impedance to its differential meaning [3].

The concept of admittance or impedance can be generalized to any domain in which energy exists under a given variety: mechanics (translation and rotation), capillarity (surface energy), hydrodynamics, thermics (heat), physico-chemistry, etc. According to Helmholtz' canonical scheme [4], in each energy variety are defined four state variables, two of them are *entity numbers*, called basic quantities q and generalized impulses p_q, the two others are *energy-per-entities*, called efforts e_q and flows f_q. For instance, in electrodynamics, the charge Q is the basic quantity q, the induction flux Φ_B is the impulse p_Q, the potential V is the effort e_Q and the current i stands for the flow f_Q. In translation mechanics, these quantities are the displacement l for the basic quantity q, the momentum $\boldsymbol{p}$ for p_l, the force $\boldsymbol{F}$ for e_l, the velocity $\boldsymbol{V}$ for f_l. In physico-chemistry, one finds the amount of substance n as basic quantity q, but there is no known variable for the physico-chemical impulse p_n; the other variables being the chemical potential μ as effort (e_n) and the substance flow (improperly called "mass flux") $\Im$ as flow (f_n). This generalization being stated, the generalized admittance $\hat{Y}_q$, in the energy variety identified by its basic quantity q, is defined as the operator, which applied to the effort e_q gives a flow f_q.

$$\text{generalized admittance,} \quad f_q = \hat{\mathbf{Y}}_q e_q \tag{5}$$

The interest of the admittance lies in the generalization brought by a definition independent from the physical process